Interaction of Iodine with Nonionic Surfactant and Polyethylene Glycol in Aqueous Potassium Iodide Solution

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When a nonionic surfactant, such as hexaoxyethylene glycol dodecyl ethers (6ED) is added to an aqueous iodine solution in the presence of potassium iodide, some spectral changes corresponding to the interaction of iodine-potassium iodide mixture with 6ED are found above the critical micelle concentration (CMC) of 6ED. The absorption maximum bands of complexes formed between 6ED and iodine are significantly different from those formed between 6ED and iodine-potassium iodide mixture in aqueous solution. The complexes of iodic compounds (such as iodine, triiodide ion and polyiodide ion) with 6ED show absorption bands at 390 nm, 370 nm and 385 nm which are assigned to an interaction between iodine-6ED, triiodide ion-6ED and polyiodide ion-6ED, respectively.

When the concentration of polyethylene glycol (PEG, MW = 200–600) becomes high in aqueous triiodide ion solution, the maximum absorption wavelength of triiodide ion solution also shifts toward 370 nm, similar to that of the triiodide ion-6ED complex.

If it is assumed that the absorbance between I_3^- and the EO chain in 6ED is the same as that between I_3^- and the EO chain of PEG, the concept of effective EO number can be applied to explain the behavior in the absorption spectra among I_3^-, 6ED and PEG. Here, the effective EO number is defined as the product of EO chain length and concentration of each 6ED and PEG in the complexes.

The effective EO number and concentration of PEG decrease in the triiodide ion-PEG complex as the molecular weight of PEG becomes large. Moreover, the effective EO number and concentration of 6ED are lower than those of PEG at all maximum absorption wavelengths.

Iodine is an electron acceptor which forms complexes with many organic compounds such as polyethylene glycol (PEG) (1,2), lipids (3,4) and nonionic surfactants (5–10). This property of iodine has been used by Ross (5) and Becher (6) for determining the critical micelle concentration (CMC) of nonionic surfactants. In their experiments, the interaction between iodine and nonionic surfactants has been explained on the basis of the charge transfer complex formation which is induced between iodine and oxygen atoms in nonionic surfactants. Similarly, iodine interacts with the oxygen atoms in polyethylene glycol or lipids to form their charge transfer complexes.

When aqueous iodine-potassium iodide solution was added drop by drop to the aqueous solution of nonionic surfactant, such as polyethylene glycol alkyl ethers, the nonionic surfactant solution became reddish. The quantity of iodine solution necessary for the reddish color was related to the number of moles of ethylene oxide in nonionic surfactants (8). Consequently, the interaction between nonionic surfactants and iodine is dependent upon the chain length of polyoxyethylene (POE) in the nonionic surfactants.

However, the change in absorption spectra of aqueous solutions of nonionic surfactant or PEG containing various ratios of iodine and potassium iodide has not been studied in detail (11–14). It is interesting to compare the interaction among nonionic surfactant, iodine and potassium iodide with that between PEG, iodine and potassium iodide. In this paper, the mole ratios of iodine and potassium iodide in their mixtures are changed in aqueous solution of nonionic surfactant, hexaoxyethylene glycol dodecyl ether (6ED), and the absorption spectra of I_2-KI mixture-6ED and I_2-KI mixture-PEG are examined in order to elucidate the mechanism of interaction of iodine and nonionic surfactants.

EXPERIMENTAL

Materials. Hexaoxyethylene glycol dodecyl ether (6ED) was supplied by Nikko Chemical Co. Ltd., Tokyo, Japan. 6ED was confirmed as highly pure by gas liquid chromatography (GLC), thin layer chromatography (TLC) and surface-tension measurements.

Iodine and potassium iodide were guaranteed grades supplied by Hikotaro Shudzui Co. Ltd., Tokyo, Japan. Iodine was purified with potassium iodide according the sublimation method. The special grade samples of glycol and polyethylene glycol were obtained from Wako Pure Chemical Industries, Ltd. , Osaka, Japan.

Water was purified by passing through a Milli-Q system (Nihon Milli Pove Co., Tokyo, Japan) until its specific condutivity fell below $10^{-7}\ \Omega^{-1}\mathrm{cm}^{-1}$.

Measurement. The absorption spectra of iodine in each sample were measured at $25 \pm 0.1\,^{\circ}\mathrm{C}$ by a spectrophotometer (Model Hitachi type 220A). All measurements were carried out within an hour after preparation of samples.

RESULTS AND DISCUSSION

In order to study the interaction of iodine with nonionic surfactant or PEG dissolved into aqueous solution of potassium iodide, it is important to elucidate the properties of iodine-potassium iodide mixture in aqueous solution. The absorption spectra of the iodine-potassium iodide mixture at 250–500 nm are shown in Figure 1 as a function of added concentration of potassium iodide. Figure 1 shows the three maximum absorption bands at 290 nm, 350 nm and 460 nm. The absorbances of iodic compounds at the three wavelengths are tabulated in Table 1. When iodine and iodide ion exist in the same solution, and the mole concentration of iodine is smaller than that of potassium iodide, the triiodide ion is formed with the following reaction (12,15):

$$I_2 + I^- = I_3^- \qquad [1]$$

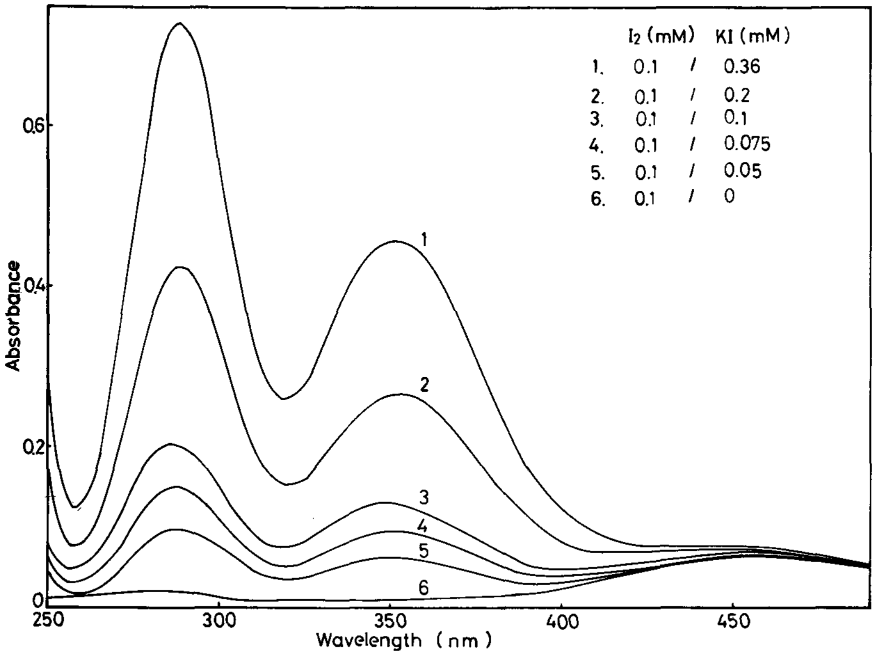

FIG. 1. The absorption spectra of iodine-potassium iodide mixture at 250–500 nm as a function of added concentration of potassium iodide.

The corresponding equilibrium constant is given by the relation (12):

$$K = [I_3^-]/[I_2][I^-] = [b-x]/x[a-(b-x)] \qquad [2]$$

where a is the original concentration of the potassium iodide, b is the total concentration of the iodine and x is the concentration of free uncombined iodine. From the data of distribution ratio of iodine between carbon tetrachloride and barium iodide solution, Pearce and Eversole (12) have found that the equilibrium constant is approximately equal to 6.0×10^{-4} in barium iodide solutions under the unsaturated condition with iodine. By using those equilibrium constant data, the concentrations of triiodide ion and of free uncombined iodine (x) are calculated and shown in Table 1.

The conditions under which equations [1] and [2] are applicable are Nos. 1–2 in the column of Table 1. The results of Nos. 1 and 2 mean that the concentrations of triiodide ion are comparatively high in these cases. This fact corresponds to the high absorbance of triiodide ion at 350 nm depending on triiodide ion.

When the concentration of iodine is higher than that of potassium iodide, the concentration of polyiodide ion becomes larger than that of triiodide ion, which is shown in No. 3–5. This reaction is shown in equation [3] (12,15):

$$nI_2 + I^- = I_{2n+1}^- \qquad [3]$$

In this case, there has been little change in the absorbance of I_2 at 460 nm (14). However, the polyiodide ion exists in the case of No. 3–5, and the absorbance of I_3^- at 350 nm (14) decreases with a decrease in the amount of I^-. It is also observed that iodine, triiodide ion and polyiodide ion coexist in this region.

The absorption spectra of iodine-potassium iodide mixture in the presence of 6ED (0.7 mM) are shown in Figure 2 as a function of added concentration of potassium iodide. The maximum absorption wavelength of iodine in the absence and presence of potassium iodide is displaced by the addition of 6ED, as shown in Figure 3. When the concentration of 6ED reaches its CMC, the maximum absorption wavelength of iodine shifts

TABLE 1

The Absorbance of Iodine-Potassium Iodide at Three Wavelengths as a Function of Added Concentration of Potassium Iodide

No.	I_2 (mM)	KI (mM)	Mole ratio	Absorbance 290 nm	Absorbance 350 nm	Absorbance 460 nm	I_3^- (mM)	x (mM)
1	0.1	0.36	1:3.6	0.7260	0.4590	0.0723	0.035	0.065
2	0.1	0.2	1:2	0.4235	0.2726	0.0703	0.023	0.077
3	0.1	0.1	1:1	0.2000	0.1320	0.0692	—	—
4	0.1	0.075	1:0.75	0.1491	0.0954	0.0646	—	—
5	0.1	0.050	1:0.50	0.0975	0.0629	0.0629	—	—
6	0.1	0	1:0	0.0186	0.0085	0.0642	—	—

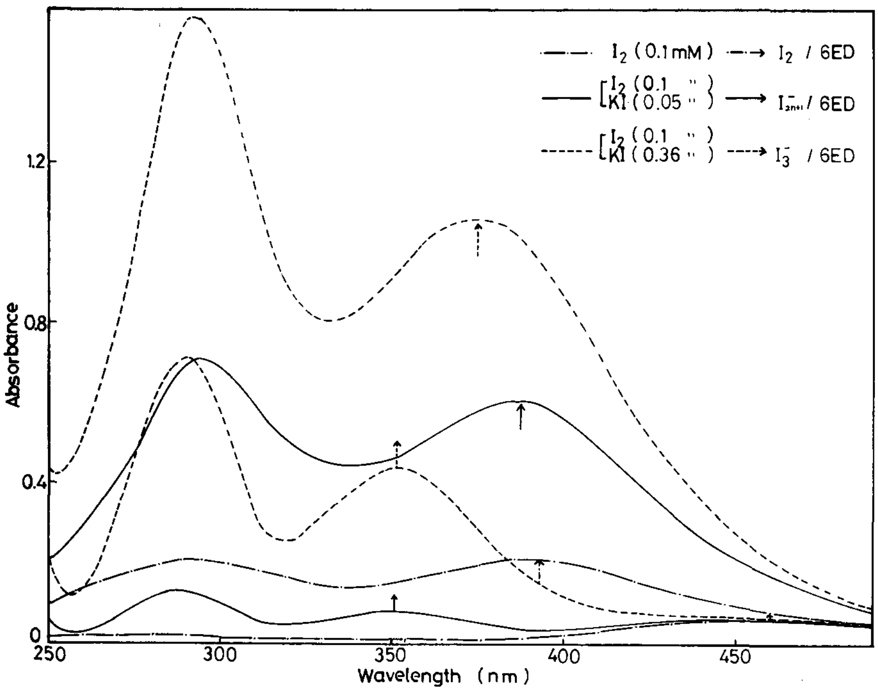

FIG. 2. The absorption spectra of iodine-potassium iodide mixture in the presence of 6ED (0.7 mM) as a function of added concentration of potassium iodide.

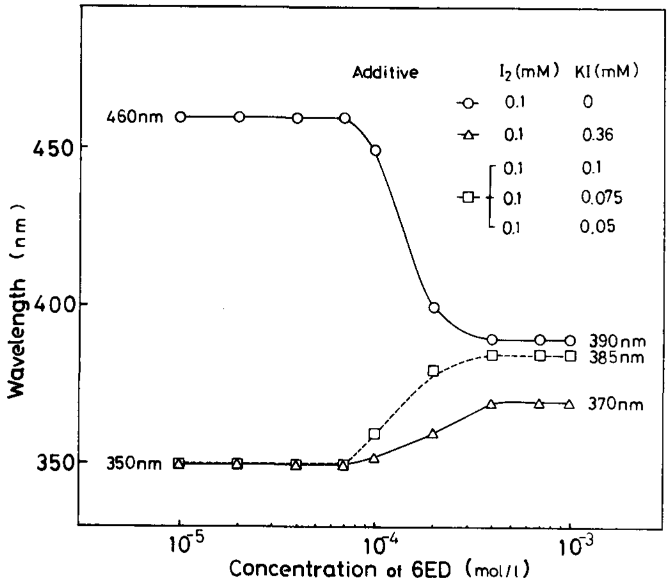

FIG. 3. The change in maximum absorption wavelength of iodine in the presence of various concentrations of potassium iodide by the addition of 6ED.

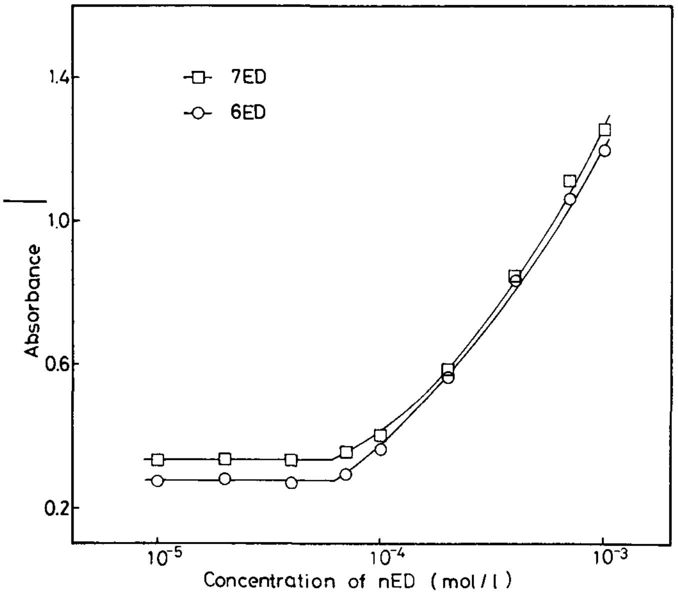

FIG. 4. The absorbance at 370 nm vs log C curves of nED in the presence of triiodide ion (I_2 = 0.1 mM, KI = 0.36 mM).

from 460 nm to 390 nm, at which the I_2-6ED complex is formed in aqueous solution.

In the case of triiodide ion, the displacement of maximum wavelength occurs from 350 nm to 370 nm depending on the I_3^--6ED complex formed by the addition of 6ED above its CMC. When the mole ratios of iodine and potassium iodide are changed to 1:1, 1:0.75 and 1:0.5, respectively, the complexes of iodic compound and 6ED are formed in every case having an absorption maximum wavelength at 385 nm. The CMC of the nonionic surfactant is not affected by the concentration of I^-.

The above results indicate that a new complex has an absorption band at 385 nm, which may consist of polyiodide ion or a mixture of iodine and triiodide ion.

Figure 4 shows the absorbance at 370 nm against log C curves of nED (n = 6,7) in the presence of triiodide ion (I_2 = 0.1 mM, KI = 0.36 mM). In the two

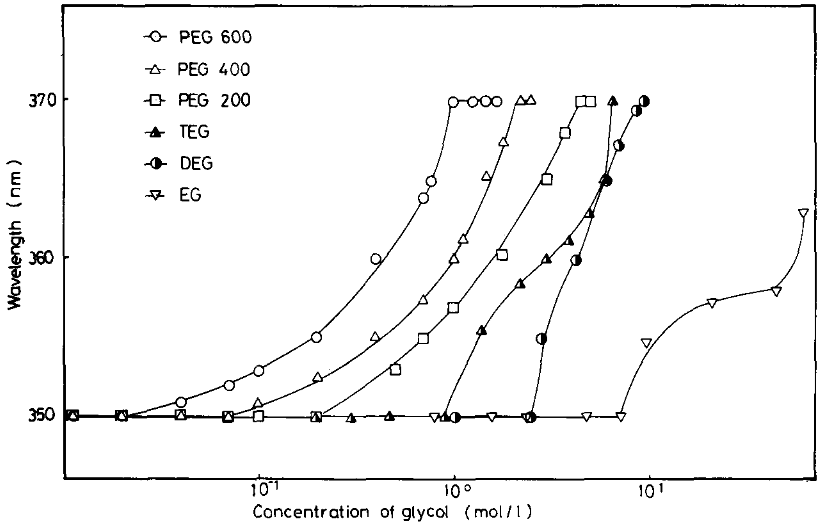

FIG. 5. The change in maximum absorption wavelength of triiodide ion (I_2 = 0.1 mM, KI = 0.36 mM) by the addition of glycol compounds with different molecular weights.

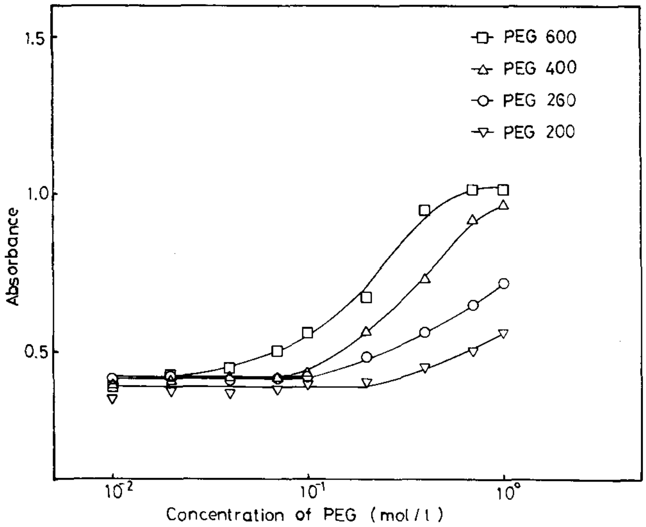

FIG. 6. The absorbance at 360 nm vs log C curves of PEG in the presence of triiodide ion (I_2 = 0.1 mM, KI = 0.36 mM) as a function of the molecular weight of PEG.

curves, break points are observed at concentrations which correspond to the CMCs of 6ED and 7ED, and the absorbance of I_3^--7ED is a little larger than that of I_3^--6ED.

Figure 5 shows that the maximum absorption wavelength of triiodide ion is displaced by the addition of glycol compounds with different molecular weights. When the concentration of PEG becomes higher, the maximum absorption wavelength of triiodide ion solution also shifts toward 370 nm, as does that obtained by the I_3^--6ED complex. The absorbances at 360 nm against log C curves of PEG in the presence of triiodide ion are shown in Figure 6 as a function of the molecular weight of PEG. These results indicate that the complex of I_3^--PEG is formed easily as the molecular weight of PEG increases.

When the complex between C_2H_4O and I_3^- is assumed to be formed at equimolar condition (1), the interaction of I_3^- with 6ED and PEG can be given by the following relation:

$$(C_{I_3^-})/(\text{EO chain length of 6ED} \bullet C_1) = (C_{I_3^-})/(\text{EO chain length of PEG} \bullet C_2) \quad [4]$$

where C_1 is the concentration of 6ED, C_2 is the concentration of PEG in the complexes and $C_{I_3^-}$ is the concentration of I_3^- in both complexes. From equation [4], the absorbance between I_3^- and the EO chain in 6ED is said to be the same as that between I_3^- and the EO chain of PEG. Now, if the concept of effective EO number is introduced to explain the absorption spectra among I_3^-, 6ED and PEG, the interpretation of equation [4] becomes more clear. Here, the effective EO number is assumed as the product of EO chain length

TABLE 2

The Effective EO Number and Concentration of PEG Compounds in I_3^- Complexes at 350 nm

Compound	PEG 200	PEG 260	PEG 400	PEG 600	6ED
Absorbance	0.4147	0.4463	0.4496	0.4530	0.4798
Conc. (M)	0.2	0.1	0.04	0.02	0.00007
Effective EO number	0.83	0.55	0.35	0.26	0.00042
	(4.1)	(5.5)	(8.7)	(13.2)	(6.0)

The number in parentheses at the bottom of each column represents the average ethylene oxide (EO) chain length for the PEG compound in that column.

TABLE 3

The Effective EO Number and Concentration of PEG Compounds in I_3^- Complexes at 360 nm

Compound	PEG 200	PEG 260	PEG 400	PEG 600	6ED
Absorbance	0.5456	0.5645	0.5684	0.5608	0.5778
Conc. (M)	0.7	0.4	0.2	0.1	0.0002
Effective EO number	2.87	2.2	1.74	1.32	0.0012
	(4.1)	(5.5)	(8.7)	(13.2)	(6.0)

The number in parentheses at the bottom of each column represents the average ethylene oxide (EO) chain length for the PEG compound in that column.

TABLE 4

The Effective EO Number and Concentration of PEG Compounds in I_3^- Complexes at 370 nm

Compound	PEG 200	PEG 400	PEG 600	6ED
Absorbance	1.6298	1.6082	1.6969	1.5015
Conc. (M)	7.0	2.0	1.0	0.002
Effective EO number	28.7	17.4	13.2	0.012
	(4.1)	(8.7)	(13.2)	(6.0)

The number in parentheses at the bottom of each column represents the average ethylene oxide (EO) chain length for the PEG compound in that column.

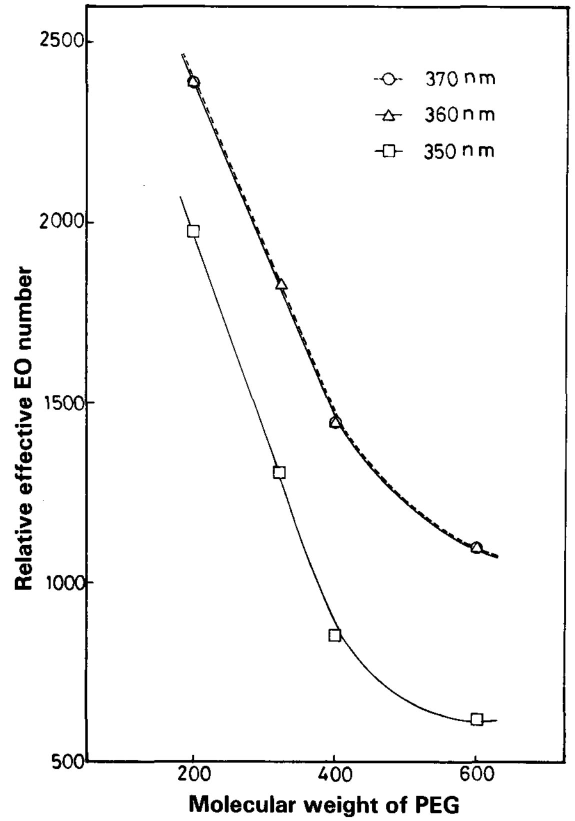

FIG. 7. The relative effective EO number of PEG at three absorption bands.

and concentration of each 6ED and PEG. The effective EO number and concentration of PEG compounds at 350 nm, 360 nm and 370 nm are shown in Tables 2–4, respectively.

The effective EO number and concentration of PEG decrease with increasing molecular weight of PEG. Moreover, the effective EO number and concentration of 6ED are lower than those of PEG at all maximum absorption wavelengths. PEG does not provide a strong effect to combine with I_3^- preferentially, unlike the polyoxyethylene in the micellar surface of 6ED. In order to compare the effective EO number of 6ED with that of PEG, the relative effective EO number can be obtained by dividing the effective EO number of PEG by the effective EO number of 6ED. These relative effective EO numbers are calculated as follows: 1976-2391 for PEG 200, 1309-1833 for PEG 260, 833-1450 for PEG 400 and 619-1100 for PEG 600, respectively (Fig. 7). The relative effective EO number of PEG decreases as the molecular weight of PEG for three absorption bands increase. This result indicates that I_3^- interacts with 6ED a thousandfold more easily than with PEG, if the same EO chain length is included in both molecules.

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